



Wet-spinning assembly of cellulose nanofibers reinforced graphene/polypyrrole microfibers for high performance fiber-shaped supercapacitors

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ARTICLE INFO

Article history:

Received 22 December 2017

Received in revised form

14 February 2018

Accepted 22 February 2018

Keywords:

Cellulose nanofibers

Graphene

Polypyrrole

Fiber-shaped supercapacitors

ABSTRACT

Fiber-shaped supercapacitors with remarkable flexibility and considerable energy-storage capacity have become the promising candidates in the field of wearable and portable electronic devices. In fact, both of the mechanical properties and electrochemical performance are in need of significant improvement to satisfy the practical applications of fiber-shaped supercapacitors. In this paper, a high-performance cellulose nanofibers reinforced graphene/polypyrrole microfiber is fabricated by a convenient wet-spinning strategy. The cellulose nanofibers act as both “enhancer” and “spacer”, which not only provide substantial hydrogen bonds to strengthen the interlaminar force but also prevent the restacking of the graphene sheets. This microfiber exhibits excellent tensile strength (364.3 MPa), which is superior to most of the reported fibers for supercapacitors. Meanwhile, the assembled fiber-shaped supercapacitors possess high specific capacitances of 334 mF cm^{-2} in liquid electrolyte and 218 mF cm^{-2} in solid electrolyte at the current density of 0.1 mA cm^{-2} , which are also at the top level of fiber-shaped supercapacitors. The presented strategy combines the industrially viable wet-spinning technology and the well-designed structure for the fabrication of high-performance ternary fiber-shaped supercapacitors, providing a good reference for the development of wearable and portable energy storage devices.

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1. Introduction

The rapid growth in the consumption of wearable electronics has stimulated many researchers to develop flexible and portable energy storage devices over the last decade [1–5]. Supercapacitors have attracted significant attention in the flexible energy storage systems, owing to their fast charge-discharge rate, high power density, long cycle life, light weight and low cost [6–9]. Fiber-shaped supercapacitors (FSCs) with unique one-dimensional (1D) structure have the advantages of the conventional two-dimensional (2D) planar supercapacitors, as well as smaller volume, higher flexibility and superior wearability than the 2D planar supercapacitors; they can be knitted into textiles and fabricated into different shapes to meet the requirements of miniaturized and diversified electronic devices [10–16]. Recently, graphene-based FSCs have been hotspots in the field of wearable electronics as a result of high power density and outstanding cycling stability

[17–19], but the low energy density due to the intrinsic electrochemical double layer capacitor (EDLC) has restrained their practical applications [20]. Therefore, various pseudocapacitive materials with high specific capacitance, such as metal oxides (MnO_2 [21], Mn_3O_4 [22] and Bi_2O_3 NTs [23]) and conducting polymers (PANI [24] and PPy [25]), are combined with graphene to achieve better performance. Among these composite FSCs, reduced graphene oxide (RGO)/polypyrrole (PPy) FSCs made by a simple method exhibit relatively high capacitance (107.2 mF cm^{-2}) and good flexibility [25]. Even so, the specific capacitance and mechanical properties of RGO/PPy FSCs are still not good enough to meet the requirements of practical applications in electronics. It is a challenge to further improve the performance of RGO/PPy FSCs.

Cellulose is one of the most abundant and sustainable natural biopolymers. Cellulose nanofibers (CNFs), which have high aspect ratios, reliable stability, excellent mechanical properties, outstanding flexibility and superior hydrophilicity, have been used as environment-friendly candidates to replace some conventional materials in the fabrication of flexible energy storage devices [26–29]. CNFs can act as a “spacer” to effectively reduce π - π stacking interactions between the graphene nanosheets, making

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the electrolyte ions penetrate deeply into the electrodes [30]. Meanwhile, the hydrogen bonds and synergistic interactions between CNFs and graphene oxide (GO)/PPy can availably enhance the mechanical performance of their composites [31,32]. Additionally, the hydrophilic CNFs in the electrode materials facilitate the absorption of electrolyte, thus ameliorating the transport of charges and improving the electrochemical performance of the supercapacitors [27,33].

Herein, we report a simple and convenient method to continuously fabricate CNFs reinforced RGO/PPy (CNFs-RGO/PPy) composite microfibers by a wet-spinning assembly strategy, in which CNFs, RGO and PPy are used as “spacer”, EDLC and pseudocapacitive materials, respectively. The ternary microfiber electrode exhibits good mechanical properties with excellent flexibility and its tensile strength can reach 364.3 MPa. The assembled symmetric FSCs possess high specific capacitances of 334 mF cm⁻² in liquid electrolyte and 218 mF cm⁻² in solid electrolyte at the current density of 0.1 mA cm⁻². Furthermore, the all-solid-state FSCs show remarkable bending stability with almost no capacitance decay after 3000 bending cycles. We attribute the outstanding mechanical and electrochemical properties to the favorable synergistic effect between CNFs and RGO/PPy.

2. Experimental section

2.1. Materials

All the reagents were of analytical grade and used as received. Bamboo powders (moso bamboo) were purchased from Zhejiang (Lishui, China) and passed through a 60-mesh sieve. GO (average lateral size ~ 5 μm, 10 mg ml⁻¹) was purchased from Hangzhou Gaoxi Technology Co., Ltd.

2.2. Preparation of CNFs

CNFs were extracted from the bamboo powders by chemical and mechanical methods according to the previous reports [34,35]. First, the bamboo powders were treated with 1 wt% acidified sodium chlorite solution at 75 °C for 1 h and then washed with deionized water until neutralized. This process was repeated 5 times to remove lignin. Second, hemicellulose in the sample was removed using 6 wt% potassium hydroxide solution at 85 °C for 2 h. Finally, a water slurry with 1 wt% undried purified sample was passed 4 times through a grinder (MKCA6-2; Masuko Sangyo Co., Ltd., Japan) at 1500 rpm. By adjusting the clearance gauge between the upper and lower grindstones (MKG-C; Masuko Sangyo Co., Ltd., Japan) of the grinder to -0.3 mm, the purified cellulose fibers were fibrillated into CNFs through high-speed shearing and extrusion during the rotation of the grindstones (Fig. S1).

2.3. Preparation of microfibers by wet-spinning

CNFs, GO and pyrrole (Py) monomers were first mixed with different weight ratio of 1:1:0.5, 1:1:1 and 1:1:2 by stirring, and then the CNFs-GO/Py mixture (~10 mg ml⁻¹) was extruded directly into a coagulation bath (0.8 wt% FeCl₃ solution containing 1 M HCl) by a syringe to fabricate continuous CNFs-GO/PPy gel microfibers. The gel microfibers were picked out after staying for several seconds and washed with 0.1 M HCl and deionized water. After drying, the microfibers were immersed in 40 wt% HI solution at 85 °C about 8 h for chemical reduction, followed by washing with ethanol and deionized water. CNFs-RGO/PPy microfibers were finally obtained after air-drying. The RGO/PPy-1 microfibers (GO:Py = 1:1, in weight) were prepared by the same procedure without adding CNFs. The RGO and RGO/CNFs microfibers (GO:CNFs = 1:0.5, 1:1,

1:2, in weight) were also fabricated by the similar methods except that CaCl₂ (5 wt%, ethanol: water = 1:3) solution was preferred as coagulation bath. According to the different weight ratio of CNFs:GO:Py, the CNFs-RGO/PPy microfibers systems were named as CNFs-RGO/PPy-0.5, CNFs-RGO/PPy-1 and CNFs-RGO/PPy-2. Similarly, the RGO/CNFs microfibers systems were named as RGO/CNFs-0.5, RGO/CNFs-1 and RGO/CNFs-2, respectively.

2.4. Preparation of flexible all-solid-state FSCs

The H₃PO₄-PVA gel electrolyte was prepared by heating the mixture of H₃PO₄, PVA and deionized water (1:1:10, in weight) with magnetic stirring until the solution became clear at 95 °C [15,36]. The ionic conductivity of the H₃PO₄-PVA electrolyte was about 4.6 × 10⁻⁴ S cm⁻¹ (Fig. S2). A layer of H₃PO₄-PVA gel electrolyte was coated on the surface of the microfibers by dip-coating method with few minutes towards solidification. An FSC was fabricated by twisting such two microfibers which were pre-coated with H₃PO₄-PVA gel electrolyte again and finally solidified at room temperature afterwards.

2.5. Characterization

Scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS) mapping images were obtained by Hitachi S-4800 field emission SEM system. Atomic force microscope (AFM) images were collected on Digital Instruments Nano Scope IIIa AFM in the tapping mode. The samples for AFM images were first dispersed in N-methyl-2-pyrrolidone and then dried on the mica sheets. Fourier transform infrared spectroscopy (FTIR) measurements were recorded on Thermo Scientific Nicolet iS10 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on Krato Axis Ultra DLD spectrometer with Al Kα radiation as the excitation source. Raman spectra were taken on Thermo Scientific DXR Raman spectrometer employing 532 nm laser source. X-ray diffraction (XRD) patterns were collected with ARL X'TRA Powder XRD System using Cu Kα radiation, λ ≈ 1.54 Å, 40 kV, 40 mA, at the scan speed of 5° min⁻¹ with a step size of 0.02°. The tensile properties were measured by SANS CMT4202 universal testing machine at a constant speed of 1 mm min⁻¹. All the electrochemical tests were conducted in a symmetrical two-electrode system, using liquid (1 M H₂SO₄) and gel (H₃PO₄-PVA) electrolytes, respectively. The effective length of each microfiber electrode was about 0.5 cm. The active mass loading of each microfiber electrode was about 1.2 mg cm⁻². Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were performed using a Chenhua CHI660E electrochemical workstation.

2.6. Calculations

The areal capacitance (C_A , mF cm⁻²), length capacitance (C_L , mF cm⁻¹) and volumetric capacitance (C_V , F cm⁻³) were calculated from the GCD curves according to the following equation:

$$C_A = \frac{2 \times I \times t}{A \times \Delta U} \quad (1)$$

$$C_L = \frac{C_A \times A}{L} \quad (2)$$

$$C_V = \frac{C_A \times A}{1000V} \quad (3)$$

where I (mA) is the discharge current, t (s) is the discharge time, A

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